

Ionic conductivity, activation volumes, and frequency-dependent conductivity in crystals with the fluorite structure

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(Received 26 November 1979)

Activation volumes were extracted from the effect of pressure on the ionic conductivities of CaF_2 , SrF_2 , BaF_2 , and CdF_2 . The activation volumes for motion of vacancies were measured in oxygen-contaminated samples and used to calculate defect-formation volumes from the activation volumes at high temperatures. The formation volumes are uniformly small and consistent with the dominance of Frenkel defects for temperatures up to 1400 K in the alkaline-earth fluorides. The CdF_2 was found to contaminate badly at temperatures around 600 K, and become an electronic conductor. All of the crystals were found to exhibit frequency-dependent conductivities at high temperatures, attributable to electrode effects or bulk dielectric response of the material, or both.

I. INTRODUCTION

Crystals with the fluorite structure have been the subjects of a great deal of study in recent years, mainly centered around their unusually high-ionic conductivities at high temperatures. We sought to investigate the conduction mechanisms in the alkaline-earth fluorides and CdF_2 by the use of hydrostatic pressure. Similar measurements on the cubic and orthorhombic phases of PbF_2 and SrCl_2 have been reported previously.¹ Measurements on the other lead halides are reported concurrently.² We will occasionally refer to equations in the latter paper to avoid repetition.

The applicability of the Frenkel model of the conductivity to the crystals with the fluorite structure is implied from doping experiments,^{3,4} and is also justified by the results of the present experiment. Therefore, we use Eqs. (4) and (5) of Ref. 2 as our model for the conductivity.

II. EXPERIMENTAL

All of the samples used were single crystals purchased from Harshaw, with the exception of some of the CdF_2 , which was purchased from Optovac Inc. Typical impurities are listed in Table I. The CdF_2 did not cleave readily, so it was broken into usable sizes. The other materials were cleaved to usable sizes. The rough pieces were then ground so that two ends were roughly parallel, and then these ends were lightly polished on fine-grit carborundum paper. Typical sample lengths varied from about 4 to 20 mm with cross sections around $3.5 \times 3.5 \text{ mm}^2$.

The electrodes were platinum buttons with a layer of graphite painted on them for the actual contact with the sample. These electrodes gave reproducible results on thermal cycling and were found to yield frequency independent resistances for frequencies in the range of 2 to 20 kHz for sample conductivities up to approximately $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. At higher tem-

TABLE I. Some typical sample impurities given in atomic parts per million.

SrF_2		BaF_2		CdF_2		CaF_2	
Ca	9000	Cu	10	La	40	Ta	30
K	80	Ti	20	Te	10	Zn	10
S	80	Cl	100	Y	20	Ni	100
P	20	S	30	Ni	120	Co	40
Si	20	Si	90	S	70	Fe	70
Na	20	Na	10	Si	30	Ti	30
						S	70
						Si	100
						Al	40
						Na	20

peratures (conductivities) the frequency dependence was so large (even at 100 kHz) that accurate data could not be obtained. This effect will be discussed later. Other electrode materials such as silver paint or evaporated platinum were tried, but were not found to yield reproducible results on thermal cycling.

Sample resistances were measured with a Hewlett-Packard model 4262A digital LCR meter. This instrument is a microprocessor-controlled meter which can make a four-wire resistance measurement, with a digitized output, in approximately 100 ms at 10 kHz. A separate control unit was built to provide for recording the temperature, pressure, and sample resistance on a teletype for later analysis. This unit allowed data to be taken automatically at present time intervals as the sample was heated or cooled. The effect of heating rate was checked to see that the sample had sufficient time to equilibrate. For heating rates from 0.5 to 12 K/min no effect was observed in the alkaline-earth fluorides. The CdF_2 contaminated so easily that it was not checked. Nearly all data were taken for heating rates less than 6 K/min. The measuring thermocouples also served as the resistance measurement leads, so that the temperature at each end of the sample could be monitored directly, and a precise mean temperature for the sample established. Details of the sample holder are shown in Fig. 1.

The high-pressure measurements were performed by the method described earlier¹ using an internally heated vessel and argon gas as the pressurizing medium. For activation volume determinations [cf. Eq. (8) of Ref. 2] resistance was measured for various pressures at constant temperature. Normally, such measurements were done on decreasing pressure to save time waiting for sample equilibration.

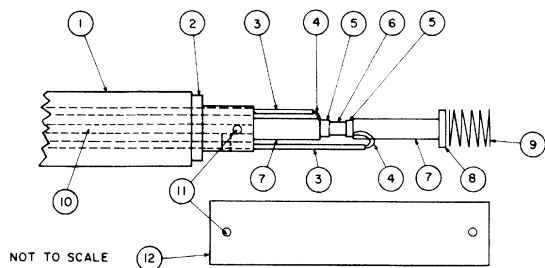


FIG. 1. Sample holder for high-pressure experiments. Holder for atmospheric-pressure measurements was similar. (1) Machined lava support. (2) Molybdenum support and sample cover holder. (3) Double-bore $\frac{1}{16}$ -in. alumina tube. (4) Platinum and platinum-10%-rhodium wires. (5) Platinum button electrodes $\frac{3}{16}$ -in. diameter. (6) Sample. (7) Alumina rod. (8) Tantalum foil. (9) Tungsten spring. (10) Molybdenum anchoring rod. (11) $\frac{1}{16}$ -in. hole for molybdenum pin. (12) Alumina sample cover.

III. RESULTS AND DISCUSSION

A. Ionic conductivity

The temperature dependence of the ionic conductivity of CaF_2 is shown in Fig. 2. The data exhibit three activated regions of conductivity, denoted I, II, and IIIB. The data were fitted to a function [by analogy with Eq. (4) of Ref. 2] of the form

$$\sigma T = A_{\text{I}} \exp\left(\frac{-\Delta E_{\text{I}}}{kT}\right) + A_{\text{II}} \exp\left(\frac{-\Delta E_{\text{II}}}{kT}\right) + A_{\text{IIIB}} \exp\left(\frac{-\Delta E_{\text{IIIB}}}{kT}\right). \quad (1)$$

Each of the exponentials in Eq. (1) corresponds to one of the three activated regions of conductivity.

By analogy with the alkali halides, region I is identified as extrinsic conduction. In most of the samples that were examined at lower temperatures, region I could be safely identified as conduction via extrinsic vacancies, because the conductivity increased after the samples had been heated to high temperatures and

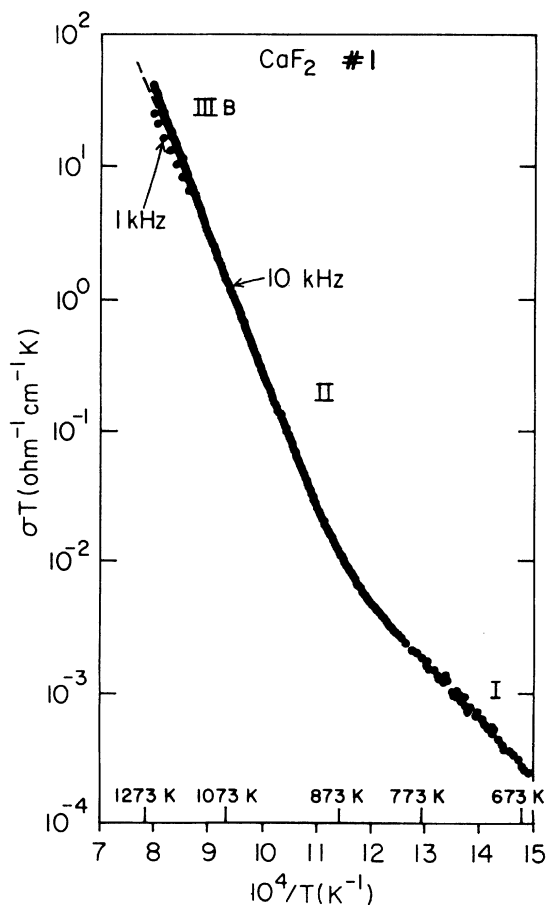


FIG. 2. Temperature dependence of the ionic conductivity of CaF_2 . Note the upward curvature and frequency dependence at high temperature.

contaminated with oxygen. The divalent oxygen would replace two monovalent fluorines, and thus leave one vacant anion site. In unused samples the identification is not so simple, as will be seen.

Doping experiments^{3,5} show that vacancies are more mobile than interstitials in CaF_2 , thus region II can be identified as conduction by intrinsic vacancies. At high temperatures a new region, labeled IIIB, appears. This region appears as an upward curvature of the conductivity, indicative of a new conduction mechanism becoming active. The most likely cause of this effect is oxygen contamination. This region could also be due to motion of the relatively immobile interstitials, or perhaps a combination of these two possibilities.

A region at the highest temperatures which would be labeled IV, is not shown in Fig. 2. This region was not observed in CaF_2 , but it was observed in most of the other fluorites. In this region the conductivity is observed to curve downward sharply from an extrapolation of region II or IIIB. This flattening appears to be the result of the concentration of de-

fects approaching a saturation point, thereby preventing the formation of additional defects. The flattening apparently takes place at a temperature just above the location of a peak in the specific heat⁶ in CaF_2 as well as in a number of other materials. This effect has been described⁶ as due to the onset of an order-disorder transition, which is inhibited by interaction of the defects before the anion sublattice becomes completely disordered.

The data shown in Fig. 2 are from a sample which was unused at the time those data were taken. The values of the parameters of Eq. (1) are given in Table II, along with some results from other work. The activation energies found for regions II and IIIB are consistent from sample to sample, while the activation energies found for region I vary from sample to sample. The value found for the data in Fig. 2 seems to be consistent with values reported for interstitial motion,^{7,8} rather than for vacancy motion, although there is a considerable spread in the reported values. All of the other data taken on CaF_2 at low temperatures (except those in Fig. 2), were taken

TABLE II. Activation energies and prefactors for anion motion in CaF_2 .

Region	Identification ^a	ΔE (eV)	Prefactor ($\text{ohm}^{-1} \text{cm}^{-1} \text{K}$)	Technique ^b	Ref.
I	ext. vac.	0.52–0.87		cond.	3
II	intr. vac.	1.02	5.6×10^9		
I	extrinsic vac.	0.55		cond.	5
I	ext. int.	1.02			
II	intrinsic vac.	1.92	7.6×10^8		
I	ext. vac.	0.38–0.47		cond.	7
II	ext. int.	0.78			
I	ext. int.	0.75–0.9		cond.	8
I	ext. vac.	0.63		cond.	9
II	intr. vac.	2.0			
II	intr.	1.96		cond.	10
II	intr.	2.00		cond.	11
I	ext. vac.	0.9		diff.	12
II	int. vac.	2.0			
I	ext. vac.	0.52 ± 0.04		cond.	Present work
I	ext. int.	0.82 ± 0.04	2.3×10^2		
II	intr. vac.	2.02 ± 0.07	1.2×10^9		
IIIB	contamination	2.4 ± 0.1	1.5×10^{11}		

^avac. is vacancy, int. is interstitial, ext. is extrinsic, and intr. is intrinsic.

^bcond. is conductivity and diff. is diffusion.

after the samples had been contaminated at high temperatures and then cooled down, and gave lower activation energies for region I, consistent with vacancy motion.

The formation energy of a Frenkel defect can be found by considering Eq. (4) of Ref. 2. The activation energy observed in the intrinsic region is the sum of the motion energy and half the formation energy. The formation energy is then found by subtracting the motion energy, deduced from region I, from the intrinsic activation energy. In CaF_2 the formation energy of a Frenkel defect is found to be $2(2.02 - 0.52)$, or $\Delta E_f = 3.00 \pm 0.16$ eV. If the anion interstitial were more mobile than the vacancy in CaF_2 then the motion energy of the interstitial would be subtracted from the intrinsic activation energy. In

that case $\Delta E_f = 2(2.02 - 0.82) = 2.4$ eV.

The conductivity data for SrF_2 can be interpreted in the same way. The data exhibit three activated regions for most samples, but a few could be reasonably well fit to two activated regions. The regions are labeled I, II, and IIIB, as for CaF_2 . It should be noted that it is not clear that region II can be safely identified as conduction via intrinsic vacancies alone. In some studies it has been found⁵ that interstitials are more mobile than vacancies in SrF_2 , so region II cannot be unambiguously identified. It may be that both vacancies and interstitials are mobile. The activation energies and prefactors, found by fitting the data to a function of the form in Eq. (1), are given in Table III. The values obtained agree reasonably well with the few other studies that have been done on

TABLE III. Activation energies and prefactors for anion motion in SrF_2 and BaF_2 .

Region	Identification ^a	ΔE (eV)	Prefactor ($\text{ohm}^{-1} \text{cm}^{-1} \text{K}$)	Technique ^b	Ref.
SrF₂					
I	ext. vac.	0.94		cond.	5
I	ext. int.	0.94			
II	intr.	1.81	2.5×10^8		
I	ext.	1.0		cond.	13
II	intr.	2.14			
I	ext. vac.	0.96 ± 0.04	5.0×10^3	cond.	Present work
II	intr.	2.10 ± 0.08	5.8×10^9		
IIIB	contamination	2.95 ± 0.12	1.1×10^{13}		
BaF₂					
I	ext. vac.	0.56	6.4×10^2	cond.	4
II	intr.	1.48	7.2×10^7		
III	intr.	1.64	6.8×10^8		
I	ext. vac.	0.59		cond.	9
II	intrinsic	2.06			
II	intrinsic	1.60		diff.	12
I	ext. int.	0.79	4×10^3	cond.	14
I	ext. vac.	0.56		cond.	15
I	ext. int.	0.76			
II	intr. vac.	1.52	1.57×10^8		
I	ext. vac.	0.62		NMR	
I	ext. int.	0.77			
II	intrinsic	1.52		cond.	16
III	intrinsic	?			
IIIB	contamination	2.1			
I	ext. vac.	0.51 ± 0.02	1.0×10^2	cond.	Present work
II	intr. vac.	1.46 ± 0.02	2.6×10^7		
IIIB	contamination	2.2 ± 0.1	1.6×10^{11}		

^avac. is vacancy, int. is interstitial, ext. is extrinsic, and intr. is intrinsic.

^bcond. is conductivity and diff. is diffusion.

this material.^{5,13} Many authors fit $\ln \sigma T$ vs $1/T$ to a series of straight lines, spanning different regions of conductivity. This procedure works reasonably well if the data can be selected very carefully, but when values are included that are in intermediate regions of the conductivity (such as between extrinsic and intrinsic), the activation energies derived will not be correct. Such errors are avoided by fitting *all* of the data to a reasonable function, such as Eq. (1). Such differences in fitting procedure may, in some cases, account for the rather large differences found for the activation energies quoted in Tables II and III.

The samples which exhibited only two regions of conductivity were those that had not been heated to as high temperatures as those which exhibited three regions. The missing region was IIIB, providing further support to the identification of this region as due to contamination by oxygen, because those samples, in which IIIB was absent, also did not show an appreciable increase in conductivity in region I at low temperatures, after they had been cooled down. The value given in Table III for the activation energy in the extrinsic region (I) was obtained for numerous samples which has been highly contaminated at high temperatures. The formation energy of a Frenkel defect for SrF_2 is found to be $\Delta E_f = 2.28 \pm 0.11$ eV.

The existence of region IV, at the highest temperatures, was observed in several SrF_2 samples. The temperature at which the fall-away of the conductivity was observed seemed to be somewhat sample dependent. A large frequency dependence of the conductivity was also found in this region, and accurate data could not be obtained. This problem will be discussed in detail in Sec. III B.

Data for BaF_2 are shown in Fig. 3, for two different samples. The lower curve was offset slightly (by a factor of 1/2.5) for viewing purposes. The lower curve is for a sample that had not previously been heated to high temperatures, while the upper curve is for a sample which had been contaminated at high temperature, as evidenced by the enhanced conductivity at low temperatures. The lower curve could be fit reasonably well to two exponentials, whereas the upper curve required three exponentials for the regions marked I, II, and IIIB. No attempt was made to try to fit the region marked IV. All four samples run exhibited region II with an activation energy of 1.46 ± 0.02 eV. Two samples were sufficiently contaminated that region I could be clearly observed. One sample exhibited a region at low temperatures with an activation energy of 0.95 eV. This was presumably intermediate between intrinsic and extrinsic, because it did not extend over a very wide temperature range. All four samples exhibited region IIIB, with an activation energy of 2.2 ± 0.1 eV.

The identification of regions I and II is fairly simple. Region I is extrinsic with conduction by anion vacancies, and region II is conduction via intrinsic va-

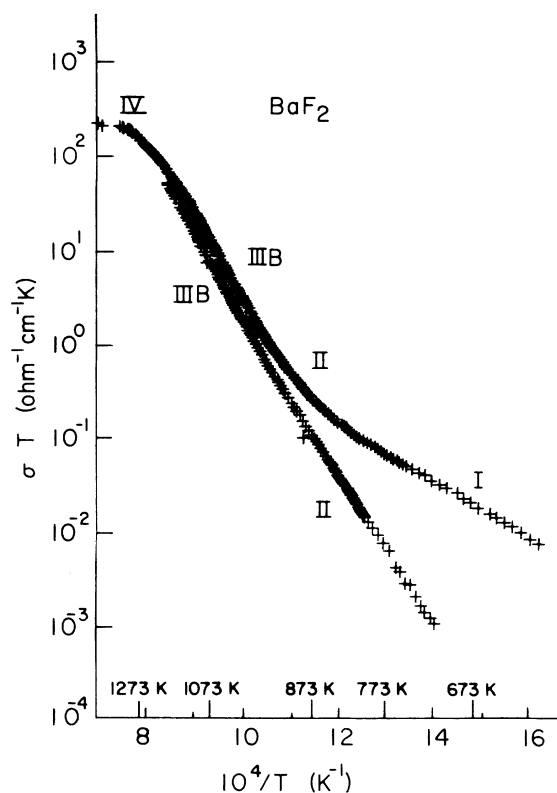


FIG. 3. Temperature dependence of the ionic conductivity of BaF_2 . Data are for two samples. (See text.)

cancies.⁴ The values of the activation energies agree reasonably well with those of other work,^{12,14-16} as can be seen in Table III. The identification of region IIIB is not so simple. The two most likely explanations for the upward curvature in this region are that it is due either to contamination by oxygen or to interstitial motion.

The possibility of interstitial motion has been suggested previously^{14,15} and can be qualitatively supported by the data shown in Fig. 3. By observing the two curves, it appears that, considering the offset, the upper curve, which is for the more contaminated sample, tends to have a slightly lower conductivity at high temperatures than the relatively uncontaminated sample, implying that the contamination causes a *decrease* in the conductivity at high temperatures. Since the contamination is with oxygen, which introduces vacancies, the decrease could be caused by recombination of mobile interstitials with the additional vacancies. If this explanation were correct, the activation energy observed for this region would be the sum of the motion energy of interstitials and half the formation energy of Frenkel defects. The energy of motion of interstitials is 0.79 eV,⁴ and the Frenkel-defect formation energy can be found from region II as $\Delta E_f = 2(1.46 - 0.51)$ eV = 1.90 ± 0.3 eV. Thus the

activation energy for motion of an intrinsic interstitial should be around 1.75 eV. This is not very close to the measured value of 2.2 eV—even allowing for a different type of interstitial motion than found in the extrinsic region. Thus, it seems more likely that region IIIB is due to oxygen contamination.

This identification of region IIIB is further supported by the work of the one other group who observed this region.¹⁶ In that work, they observed *all* of the regions II, III, IIIB, and IV. They noted an upward curvature signifying region III, but they did not have sufficient data to obtain an activation energy. They also observed an even more obvious upward curvature signifying region IIIB with activation energy 2.1 eV, and they identified this as due to contamination. The region IV they observed is where the curve flattens at high temperature. If the contamination is the cause of region IIIB, no solid evidence is found in the present work for the existence of region III, i.e., an intrinsic region possibly due to motion of interstitials.

It may also be noted that the conductivity of the upper curve in Fig. 3 flattens into region IV sooner than the lower curve. This effect is most likely caused by the frequency dependence of the conductivity observed at high temperatures in this material, as well as most of the others examined. The frequency dependence will be discussed in more detail in Sec. IIIB. One clue to the explanation for the observed effect is that it is apparently related to the sample dimensions. The data for the upper curve in Fig. 3 are from a sample which was only about half the length of the sample represented by the lower curve.

Some typical data exhibiting the temperature dependence of the ionic conductivity of CdF₂ are shown in Fig. 4. The behavior at low temperatures appears typical for an ionic conductor. The data nor-

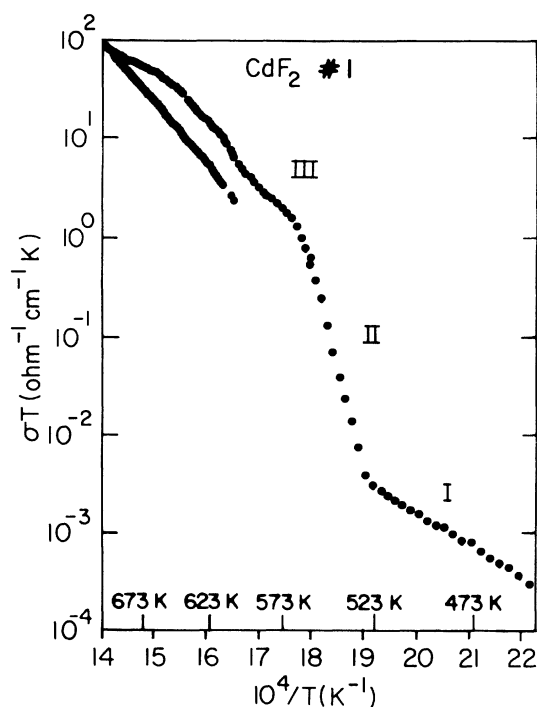


FIG. 4. Temperature dependence of the conductivity of CdF₂.

mally exhibited an association region (not shown in Fig. 4), an extrinsic region I, an apparent intrinsic region II, and another region labeled III. At higher temperatures the behavior was inconsistent from one sample to another, probably due to the severe contamination in this material. The crooked curve found above region III was taken on increasing temperature, while the straight portion (lower curve) was taken on decreasing temperature. The form of the curve in Fig. 4 is generally consistent from sample to sample, but the activation energies obtained for the

TABLE IV. Activation energies for CdF₂.

Sample	Region	Activation energy (eV)	Technique ^a	Ref.
1	I	0.60	cond.	Present work
2	I	0.74		
3	I	0.62		
1	II	4.15		
2	II	4.68		
3	II	2.52		
1	III	1.00		
2	III	0.73		
3	III	1.32		
	I	0.39	diff.	17
	II	1.44		
	I	0.52 (varied)	cond.	18
	II	2.64		

^acond. is conductivity and diff. is diffusion.

various regions varied. Values for the activation energies found for three samples are given in Table IV along with values from other work.

The conductivity and diffusion experiments clearly disagree markedly. The diffusion data indicate that region II does not appear until nearly 500 °C,¹⁷ while the conductivity data indicate its appearance at around 300 °C.¹⁸ The temperature at which region II appears is certainly impurity concentration dependent, but this difference is unusually large.

Because diffusion studies indicate only the fluorine motion while conductivity depends on motion of all charged species, the interpretation of regions I, II, and III is then more straightforward. The conductivity in region I is probably due mostly to motion of fluorine vacancies. Region II is partly due to conduction by fluorine vacancies and partly by something else, probably electrons. The behavior of the conductivity above region II is probably dominated by electron transport, which is apparently related to the contamination of the sample. Support for this explanation comes from these sources: the pressure measurements, which will be discussed in Sec. III C; measurements of the conductivity of samples at various stages of contamination, indicating that the activation energy observed in all regions decreased each time the sample was heated up, eventually reaching a single value of about 0.05 eV from room temperature up to approximately 400 °C, much too small to be consistent with fluorine motion; the fact that CdF₂ can be easily converted to a semiconductor by heating it in Cd vapor.^{19,20} Therefore, the activation energies observed in regions II and III are not interpretable in terms of the Frenkel-defect model.

B. Frequency-dependent conductivity at high temperatures

1. Electrode effects

All of the crystals with the fluorite structure that were examined exhibited a frequency-dependent conductivity at high temperatures. The data shown in Fig. 5 for SrF₂ illustrate the effect. It is clear that this effect tends to obscure the observation of region IV in the conductivity data. The measured value for the conductivity decreases as the frequency of the measuring current is decreased. Thus, the temperature at which region IV appears (the conductivity begins to reach saturation), may seem to be at a lower temperature than it should be, and the leveling off of the conductivity may appear to be more severe than for the inherent conductivity. Apparently, the frequency-dependent conductivity has only been noted once previously in the fluorites¹⁵ and was not studied. Such an effect was also recently reported in work on LaF₃,²¹ but it also was not studied in detail.

The frequency dependence of the conductivity be-

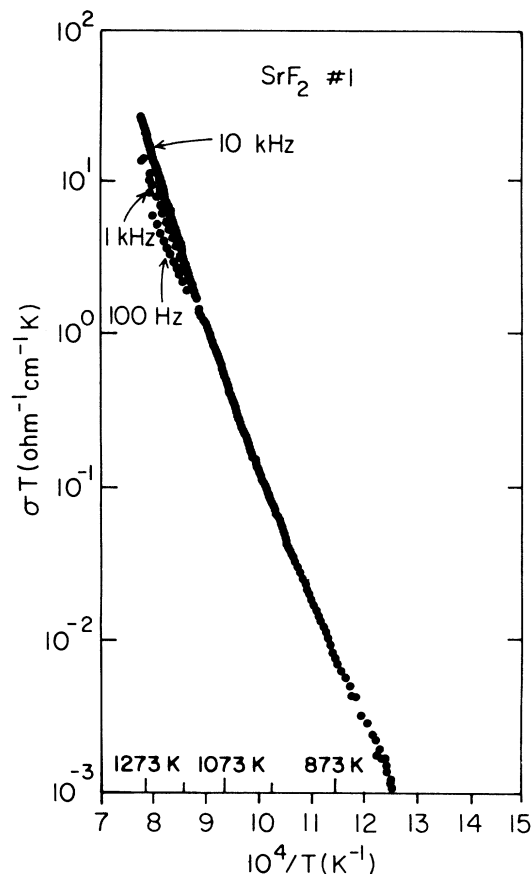


FIG. 5. Frequency dependence of the conductivity at high temperature. Data are for SrF₂, but other materials behave similarly.

comes important at temperatures around 850 °C (or conductivities of about 10⁻³ ohm⁻¹ cm⁻¹) in the alkaline-earth fluorides. The effect depends on sample dimensions. The magnitude of the measuring current is much less important than the frequency. The measured resistance was reduced by about 20% when the measuring current was reduced from 1 mA to 50 μA (a factor of 20), at 10 kHz, while for a sample resistance of about 60 ohms at 10 kHz, the resistance increased by as much as 200% in changing to 1 kHz and decreased by about 15% in going to 100 kHz (all at 50 μA).

This is not a new problem.²²⁻²⁶ A likely cause of the observed effects is electrical polarization of the sample at the electrode interface. During one-half of the applied current cycle ions can be swept out of the crystal face into small pockets between the sample and the platinum electrodes. During the next half cycle of the current, some, but not all, of the fluorine or chlorine can be swept back into the sample. After a short time (probably a few cycles) the sample and gas in the interface region reach equilibrium for a

given applied frequency. The result of this polarization is to leave a layer of the sample depleted of charge during each half cycle of the applied current. It is possible to represent this effect as a parallel-plate capacitor with area about equal to that of the sample face and with plate separation l about equal to the diffusion distance of the ions during one-half cycle of the applied current. The diffusion distance is $l \sim (D/2f)^{1/2} = (D\pi/\omega)^{1/2}$, where D is the diffusion coefficient and $f = \omega/2\pi$ is the measuring frequency. The impedance due to the polarization would then be proportional to $\omega^{-1/2}$. A more careful analysis^{22,23} shows that the "diffusional" impedance Z_2 is given by

$$Z_2 = (2\sqrt{2}z^{-2}F^{-2}c_0^{-1}D^{-1/2}RT)(1+i)^{-1}\omega^{-1/2} \\ = K_2^{-1}\omega^{-1/2}(1+i)^{-1}, \quad (2)$$

where z is the number of charge units on the diffusing ion species, F is the Faraday constant, c_0 is the concentration of diffusing species, R is the gas constant, and $i = \sqrt{-1}$.

When the sample resistance is low ($\leq 500 \Omega$), the measuring instruments output the equivalent series circuit parameters, R_{EQ} and C_{EQ} , as shown in the upper diagram in Fig. 6. The equivalent circuit shown at the bottom of Fig. 6 is taken from Ref. 26 and is a better representation of the physics. The parameters R_1 and C_1 represent the bulk resistivity and geometrical capacitance of the sample. Z_2 represents the diffusional impedance of Eq. (2) and C_2 represents the additional effect, inherently coexisting with the diffusional impedance of space charge present in the sample near the interface. R_3 and C_3 represent hindered electron transfer in the interface region and interface adsorption of the mobile ions, respectively. The lower circuit in Fig. 6 is still not

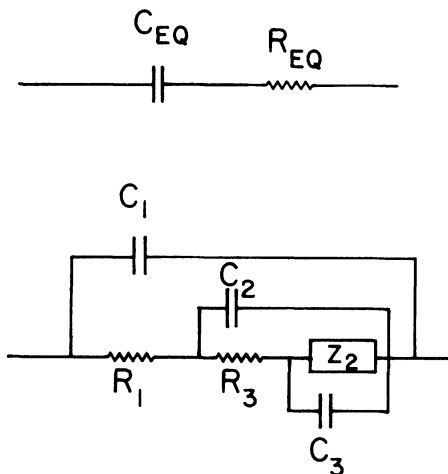


FIG. 6. Equivalent circuit for conductivity measurements. The upper circuit represents the parameters obtained from measuring instruments for low-resistance samples. The lower circuit is the equivalent circuit suggested in Ref. 26.

completely correct because it does not allow for dc conductivity that was observed if Z_2 is given by Eq. (2).

The present study indicates that measuring frequencies higher than 100 kHz are required if the frequency-dependent conductivity is to be at all avoided. The limit of the apparatus available was 150 kHz.

2. "Universal" dielectric response

The fact that the observed frequency dependence does not scale with the measuring current suggests that the electrode problems may not, in fact, be the real cause of the observed behavior. Jonscher²⁷ has suggested that a frequency dependence is a bulk phenomenon, quite apart from electrode problems. He noted that a wide variety of materials exhibit frequency dependent conductivities of the form

$$\sigma \propto \omega^n, n \leq 1 \quad (3)$$

and was able to account for this dependence in terms of many-body contributions to the imaginary part of the dielectric constant.²⁸ This theory is normally applied to good dielectrics (σ small), but it seems to be applicable to other materials as well.²⁷ The form of Eq. (3) is found to describe hopping conduction in $\text{Na-}\beta\text{Al}_2\text{O}_3$ (a superionic conductor) at low temperatures as well as hopping conduction in amorphous silicon (electronic conductor). In good dielectrics it is found that values of n in the range 0.5 to 0.9 are associated with charge transport by extrinsic carriers with values closer to unity are typical of intrinsic behavior. Values of n in the range 0.1 to 0.3 are typical of high-carrier-density solids at low frequency (~ 10 Hz).²⁸

The high-temperature data in Fig. 3 could be fit to the form of Eq. (3). The resulting values of the exponent, n , at each temperature are given in Table V. The exponent appears to be temperature dependent: the values shown in Table V can be fit to a straight line, $n = -1.10 \pm 0.07 + (1.027 \pm 0.060)T$.

It is interesting that the frequency-dependent data obtained in the high-temperature regions for a number of different samples could all be reasonably

TABLE V. Exponent n from Eq. (3) for various temperatures in SrF_2 .

T (K)	n
1195	0.122
1205	0.138
1213	0.148
1222	0.154
1231	0.166
1242	0.173
1252	0.183

well fitted by Eq. (3) with values for the exponent in the range 0.006 to 0.26. These values are certainly within Jonscher's limits for a "high-carrier-density" solid (although at relatively high frequencies) and clearly supportive of this theory. However, it is not clear that the observed dependence of the conductivity on sample dimensions and on pressure can be explained by this theory. The frequency dependence observed in our samples may, in fact, be a result of a combination of electrode (polarization) effects and bulk dielectric response.

C. Activation volumes

The activation volumes were found from the pressure dependence of ionic conductivity by use of Eq. (8) of Ref. 2. The Grüneisen parameters and compressibilities of the alkaline-earth fluorides were taken from Ref. 29. The transverse-optic-mode Grüneisen parameters were used as the most reasonable choice, but the fact they are of order unity makes the choice relatively unimportant. The available compressibility data were linearly extrapolated to higher temperatures from the values found at 77 and 300 K. Recent results from Brillouin-scattering experiments³⁰ on SrCl₂ show that this is not a bad choice until the temperature reaches the region of the peak in the specific heat where the elastic constants fall off faster than linearly. The data were not corrected for this effect. The elastic constants used would give the adiabatic compressibility, whereas the isothermal compressibility is needed. The difference is fairly small,³¹ and since the term in which the Grüneisen parameter and compressibility appear was generally less than 10% of the other term these uncertainties are of slight importance.

The activation volumes of CaF₂ are shown plotted against absolute temperature in Fig. 7. The two points at the lower left corner of the figure were taken on highly contaminated samples, and they represent the activation volume for vacancy motion in CaF₂. The average value obtained is 2.1 ± 0.7 cm³/mole, which compares well with a recent study of the effect of pressure on dielectric relaxation in CaF₂,³² indicating a motion volume for associated vacancies of 1.73 ± 0.1 cm³/mole. The activation volume increases markedly with increasing temperature. The values found between 700 and 1050 K agree with the only other values available for CaF₂.³³ The values above 1050 K are new. The best value for the intrinsic activation volume is probably at about 1050 K. This temperature is high enough that the low-temperature extrinsic region is no longer influential (hence the intermediate volumes between 700 and 1000 K), and low enough that the contamination and frequency dependence occurring at high temperatures do not become important. Thus, the intrinsic activation volume is 7.0 ± 0.5 cm³/mole.

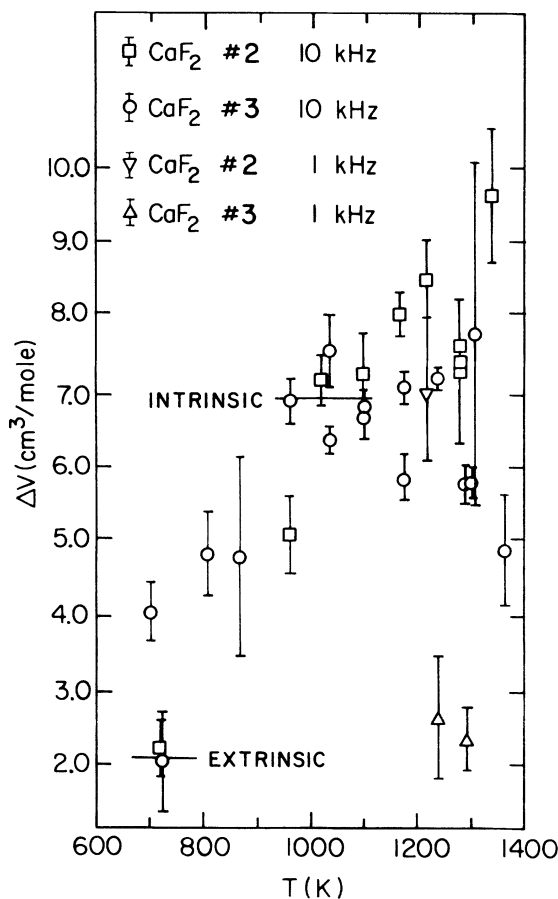


FIG. 7. Activation volumes for CaF₂.

The formation volume of Frenkel defects, ΔV_f , is then $2(7.0 - 2.1)$ cm³/mole, or $\Delta V_f = 9.8 \pm 1.6$ cm³/mole. This value is small compared to the molar volume of CaF₂ of 24.6 cm³/mole, and therefore justifies the presumption of a Frenkel-defect mechanism.

The interpretation of the data at temperatures above 1100 K is obviously difficult, considering the large spread in values observed. This is the region where the frequency dependence of the conductivity becomes important, as well as the oxygen contamination. First consider just the open squares. Between 1100 and 1350 K they show a general increase in the activation volume from 7 to about 9.5 cm³/mole, probably due to the increasing contribution of the contaminating oxygen to the conductivity. Note that the value given by the inverted triangle is for the same sample, only using a measuring frequency of 1 kHz instead of the usual 10 kHz. The value is lower, but not too much. Now, consider just the open circles. These values also show an increase in the activation volume, but the increase stops at about 1200 K, where the volume begins to decrease. Also note the two points at lower right represented by triangles.

These values are for the same sample as the open circles, but at 1 kHz, indicating that the various effects contributing to the frequency dependence are also pressure dependent.

The explanation for the difference between the squares and circles lies in consideration of the sample dimensions. The sample called 2, represented by the squares, had approximately the same length as sample 3 (~ 8 mm) but its cross-sectional area was less than half that of sample 3. The capacitive effects at the electrode were presumably that much smaller, resulting in a smaller error in the measured resistance.

The activation volumes for SrF_2 are shown in Fig. 8. The values at the lower left were taken after the samples had been contaminated at high temperatures, so the value represented by the triangle is the activation volume for motion of vacancies. This value, $\Delta V_m(\text{vac}) = 3.3 \pm 0.3 \text{ cm}^3/\text{mole}$, agrees well with the only other value available of $3.2 \text{ cm}^3/\text{mole}$.³³ The volumes between 900 and 1100 K are in the intermediate range between extrinsic and intrinsic conduction. We take the average value at about 1150 K as the best representative of the intrinsic value for the

samples studied, $7.5 \pm 0.5 \text{ cm}^3/\text{mole}$. If the intrinsic conduction is by vacancies, then the formation volume of Frenkel defects, ΔV_f , is $8.4 \pm 1.1 \text{ cm}^3/\text{mole}$. The activation volumes at higher temperatures are from the contamination region IIIB. Some data were also taken at 1 kHz and are not shown. Those values also show a drop in the activation volume, similar to that observed for CaF_2 .

The possibility that the intrinsic conductivity in SrF_2 is dominated by interstitial motion is made less likely by recent results on the effect of pressure on associated interstitials.³⁴ These results show a higher activation volume for motion of interstitials than for vacancies. They obtain $\Delta V_m(\text{int.}) = 4.7 \pm 0.1 \text{ cm}^3/\text{mole}$. This value would give a formation volume of $5.6 \text{ cm}^3/\text{mole}$. In either case the formation volume is small compared to the molar volume of $29.3 \text{ cm}^3/\text{mole}$ and therefore consistent with the dominance of Frenkel defects.

The activation volumes of BaF_2 are shown in Fig. 9. Beginning with the open squares and solid squares, the activation volumes of these two previously unused samples are all near $5.6 \pm 0.3 \text{ cm}^3/\text{mole}$ in the temperature range of 800 to near 1150 K,

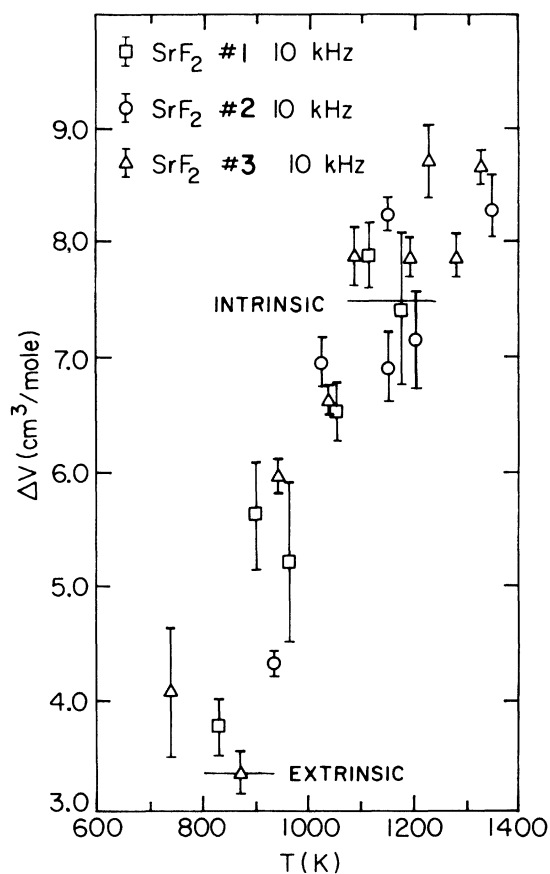


FIG. 8. Activation volumes for SrF_2 .

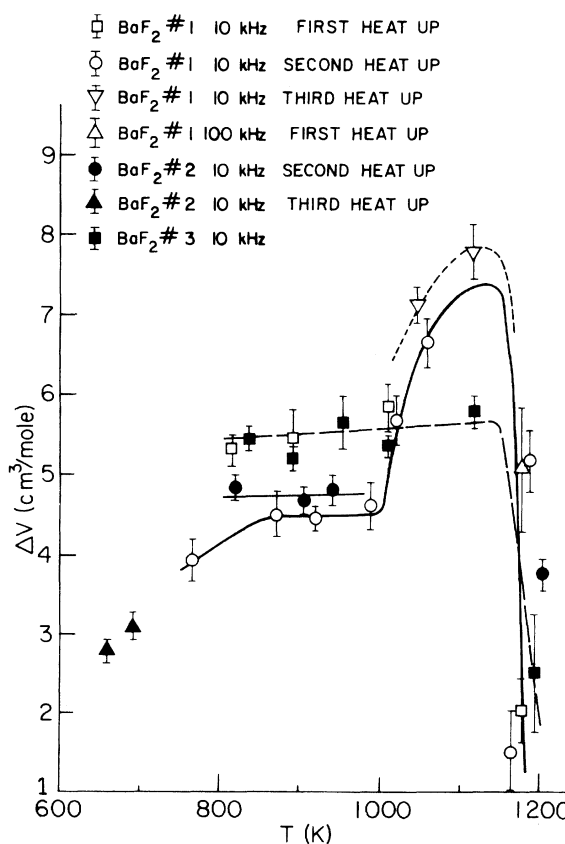


FIG. 9. Activation volumes for BaF_2 .

where a sudden decrease is observed. The value $5.6 \text{ cm}^3/\text{mole}$ compares reasonably well with the only other available values³³ of $5\text{--}6 \text{ cm}^3/\text{mole}$. When one of those samples was heated again, the values shown by the open circles were obtained. At temperatures below 1000 K the activation volumes decrease to values that are apparently typical of the region between extrinsic and intrinsic, indicating that appreciable contamination had occurred during the first measurements. Near 1025 K the intrinsic activation volume is obtained and above 1050 K the activation volume increases further. The volumes again tend to decrease at temperatures above 1150 K . During the third heating of the same sample the volumes represented by the inverted triangles were obtained. These values of the activation volume represented by the inverted triangles and open circles, above $6.5 \text{ cm}^3/\text{mole}$, are probably representative of the contamination occurring at these high temperatures. Other values, represented by the solid circles, are for another sample during the second heating. (The results of the first heating were similar to those values shown for the other samples.) The volumes obtained during the third heating of one sample are shown at the lower left by the solid triangles. These values are probably the extrinsic values, representing the activation volume for motion of vacancies; i.e., $\Delta V_m(\text{vac.}) = 3.0 \pm 0.3 \text{ cm}^3/\text{mole}$. The point shown by the open triangle at 1180 K represents the activation volume obtained when a 100-kHz measuring frequency was used. This value should be compared with the value, at the same temperature, represented by the open square. Another point that was taken at 100 kHz is shown at 1285 K . These two points taken at 100 kHz tend to indicate that the falloff of the activation volume above 1125 K is related to the frequency dependence of the conductivity. All of the points taken above approximately 1125 K are in the region where the frequency dependent conductivity was observed.

We can find the Frenkel-defect formation volume, ΔV_f , from the intrinsic activation volume and the motion volume of vacancies; i.e., $\Delta V_f = 2(5.6 - 3.0) \text{ cm}^3/\text{mole} = 5.2 \pm 0.4 \text{ cm}^3/\text{mole}$, again small compared to the molar volume of 36.3 cm^3 .

The activation volumes of CdF_2 are shown in Fig. 10. The exact interpretation of these data in terms of the Frenkel-defect model is questionable, for the reasons noted earlier. However, the trend of the data is clear. There is an apparent increase in the activation volume at temperatures up to about 600 K . Between 600 and 650 K there is a sudden increase in the activation volume, which even goes negative for some samples.

While the activation volume cannot be interpreted in terms of the reaction-rate theory of diffusion, because of the apparent electronic contribution, it still is a valid measure for the pressure dependence of the

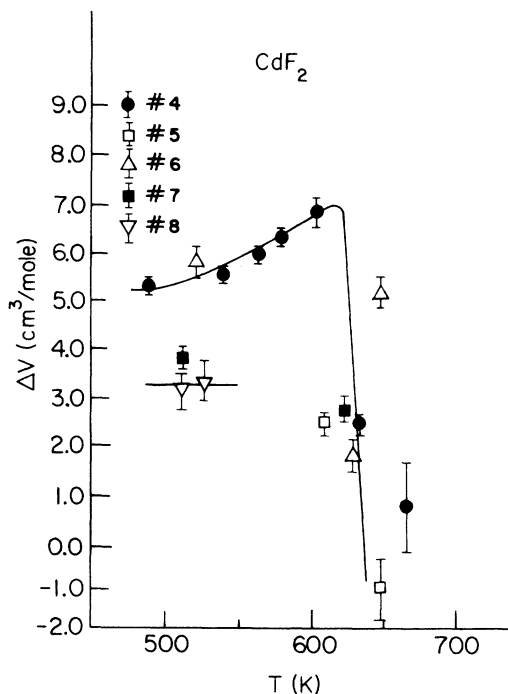


FIG. 10. Activation volumes for CdF_2 .

conductivity. Large activation volumes correspond to a large pressure effect; small volumes correspond to a small pressure dependence, such as would be expected for an electronic conductor. Negative volumes indicate that increased pressure increases the conductivity.

The temperature at which the activation volumes decrease is in the range where the conductivity and diffusion data disagree. Therefore, it is consistent that the activation volume should decrease, if electronic conduction is beginning. The samples which exhibited negative activation volumes were the same samples which were very highly contaminated (all samples were contaminated, these were the worst). Auger electron spectroscopy demonstrated that these samples were contaminated to at least 10^4 \AA into the bulk with oxygen and some silicon. They also had a yellowish color—typical of CdO . Two explanations for the enhanced conductivity under pressure seem reasonable: the material may be a semiconductor with a narrow gap that becomes even narrower as pressure is increased; a second possibility, suggested by the yellow coloration, is that oxygen contamination introduces vacancies on the anion sublattice which then trap electrons to become F centers (or some other color center). The enhanced conductivity under pressure could then be due to hopping motion of electrons from F centers to empty vacancies, which would be somewhat more likely with smaller lattice parameters accompanying the high pressure.

The low-temperature activation volumes probably can be interpreted as the result of the effect of pressure on fluorine motion. If this is true, then the activation volume for motion of fluorine vacancies is approximately $3.1 \pm 0.2 \text{ cm}^3/\text{mole}$. This value is represented by one of the open inverted triangles at about 510 K. The activation volumes found between 5 and $6 \text{ cm}^3/\text{mole}$ are probably representative of the region between extrinsic and intrinsic conduction. The value of $6.5 \pm 0.5 \text{ cm}^3/\text{mole}$ is most likely to be typical of the intrinsic conduction. These values result

in a Frenkel-defect formation volume, $\Delta V_f = 6.8 \pm 1.1 \text{ cm}^3/\text{mole}$.

ACKNOWLEDGMENTS

We wish to thank A. B. Lidiard for helpful discussions and for pointing out the work of A. K. Jonscher to us. We also thank L. E. McNeil for her invaluable assistance in the lab and J. Schoonman for his helpful comments on electrode problems. This work was supported in part under Department of Energy Contract No. EY-76-C-02-1198.

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